

Materials Science

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Thermal conductivity of solids from lattice dynamics

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Heat transport is a fundamental process underlying both natural phenomena and technological advancements. In semiconductors and insulators, where heat is primarily carried by lattice vibrations, the lattice thermal conductivity (κ_L) plays a crucial role in governing thermal transport. Lattice dynamics provides a robust theoretical framework for calculating κ_L , with different approaches tailored to the structural and morphological characteristics of materials.

Solids can be broadly classified into crystals, glasses, and partially disordered solids, with a continuous crossover between these categories (see Figure 1). In crystalline semiconductors and insulators, heat is primarily carried by phonons. The phonon-gas model (PGM), introduced by Peierls in 1929, reliably predicts κ_L in simple crystals, ranging from ~ 1000 W/mK for boron arsenide to 0.9 W/mK for silver chloride at 300 K. In glasses, strong atomic disorder breaks down the phonon definition, making the PGM unsuitable for computing glassy κ_L . To address this, Allen and Feldman [1] proposed the AF model in 1993, which describes the glassy heat transport in harmonic glasses through Zener-like tunneling between quasi-degenerate vibrational eigenstates.

However, exceptions to these models exist. In certain complex crystals with glass-like heat conduction, such as Ti_3VSe_4 [2], severe phonon scattering reduces the phonon mean free path below the minimum interatomic spacing, significantly limiting phonon propagation. As a result, κ_L of Ti_3VSe_4 computed using the PGM substantially underestimates experimental results [2]. Moreover, the transition from crystals to glasses is nonsharp, with partially disordered materials [3] occupying an intermediate regime where heat transport cannot be accurately described by either the PGM or the AF model.

In 2019, Simoncelli *et al.* [4] introduced the Wigner transport equation (WTE) to describe heat conduction in solids, incorporating both intraband propagation (κ_P) and interband coherence (κ_C) via Zener-like tunneling. This framework unifies particle-like phonon propagation (dominant in crystals) and wavelike phonon coherence (dominant in glasses), and the overall κ_L is the summation of κ_P and κ_C . Later, Isaeva *et al.* [5] developed the Quasi-harmonic Green-Kubo theory (QHKG), which is also applicable to both crystalline and glassy solids. A detailed comparison between WTE and QHKG can be found in previous studies [6, 7].

Specifically, in simple crystals with moderate anharmonicity, where κ_L typically follows a T^{-1} dependence, WTE and QHKG predict that the heat transport is dominated by particle-like phonon propagation, with wave-like tunneling effects being negligible. In contrast, in complex crystals with strong anharmonicity, where closely spaced vibrational frequencies and large phonon linewidths lead to significant phonon mode overlap (see Figure 1), WTE and QHKG predict a substantial interband coherence contribution ($\kappa_C \approx \kappa_P$), resulting in glass-like κ_L with a weakened T -dependence. In extreme cases, where κ_C dominates heat transport in crystals, κ_L can even increase with temperature.

For partially disordered solids and glasses, calculating κ_L requires sufficiently large atomistic models to capture atomic disorder. Once the model is large enough to represent the amorphous structure, further increases in system size or changes in boundary conditions have minimal impact on κ_L . Therefore, computing κ_L for disordered solids is computationally expensive

Unified thermal transport theories for solids

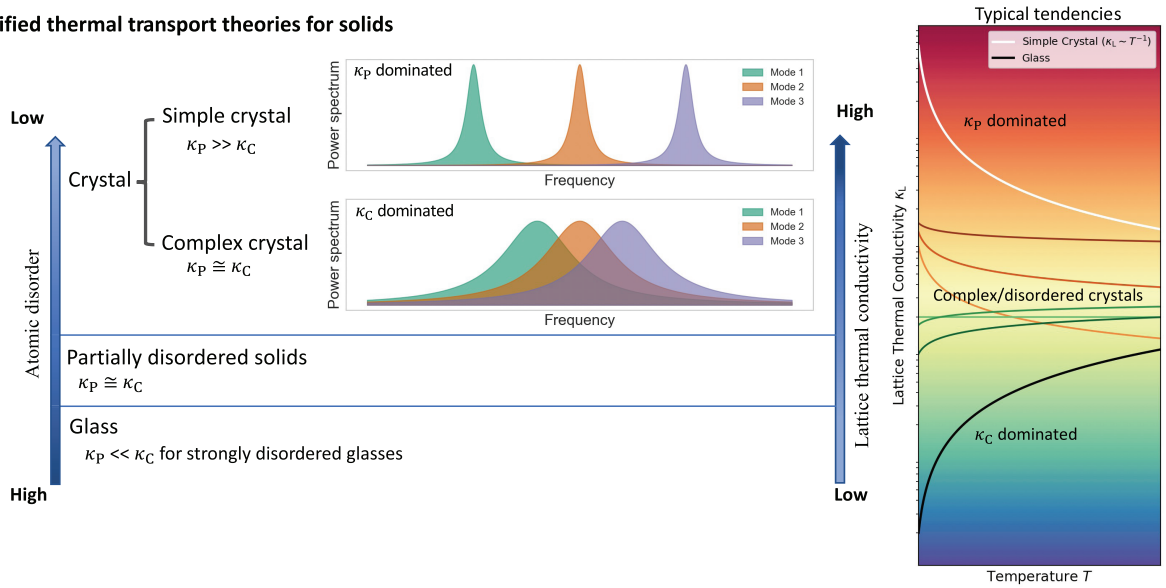


Figure 1 Classification of solids and their heat transport mechanisms. The left panel categorizes solids based on atomic disorder, ranging from simple and complex crystals through partially disordered solids to glasses. The corresponding vibrational power spectra illustrate the transition from well-separated phonon modes in simple crystals to overlapping modes in complex crystals due to phonon broadening. The right panel depicts the typical temperature (T) dependence of lattice thermal conductivity (κ_L) across different solid categories, highlighting the transition from κ_P -dominated transport in simple crystals to κ_C -dominated transport in disordered glasses.

and labor-intensive. To overcome this challenge, the regularized WTE (rWTE) approach [8] was developed to accelerate κ_L calculations in strongly disordered glasses by using a relatively small atomic model with Fourier interpolation. This method is particularly effective when disorder-induced repulsion between vibrational energy levels is comparable to the intrinsic linewidths from phonon-phonon scattering or isotopic scattering.

Although WTE and QHGK are powerful tools for assessing heat transport in solids, they have inherent challenges and limitations. A key challenge arises in glasses, where the interplay between anharmonicity and disorder complicates the convergence of κ_L . The AF model predicts a finite κ_L for harmonic glasses at low temperatures. However, Fiorentino *et al.* [9] emphasized that incorporating anharmonic linewidths in QHGK is essential for achieving convergence. Recent studies [10] have shown that κ_L can converge in harmonic disordered systems if the disorder is not simple white-noise mass disorder and the disorder-induced phonon lifetimes deviate from Rayleigh scattering at low frequencies. We emphasize that further research is needed to better understand the interplay between atomic disorder (nearly T -independent) and anharmonicity (T -dependent) in glasses.

WTE and QHGK have limitations in their applicability. Both methods require phonons to be well-defined quasiparticles, meaning their linewidths must be smaller than their energies. This assumption breaks down in strongly anharmonic solids with ultralow κ_L , where phonon linewidths become comparable to or exceed their energies. Similarly, in halide perovskites with low-frequency overdamped modes, the phonon power spectrum deviates significantly from a Lorentzian shape, exhibiting imaginary frequencies that render linewidth extraction unreliable. In such cases, the full phonon spectral function method [6] on top of WTE may provide a more accurate prediction of κ_L .

Additionally, WTE and QHGK assume that atoms vibrate around well-defined equilibrium positions (i.e., need a stable initial atomic model to compute κ_L). However, this assumption often fails in metastable materials with frequent atomic hopping and spinning or in phase-change materials transitioning between amorphous and crystalline states. These materials feature a complex energy landscape with multiple metastable states, resulting in dynamic atomic rearrangements. Accurately modeling heat transport in such systems requires more advanced computational approaches beyond existing methods.

Challenges and opportunities coexist. The recent advancements in machine learning and artificial intelligence are making the implementation and application of existing heat transport theories increasingly feasible. Future efforts may focus on developing more general theoretical frameworks to address unconventional and unresolved heat transport phenomena across

diverse materials. We anticipate that emerging heat transport theories will continue to deepen our understanding of transport mechanisms in complex systems, such as solid-liquid interfaces and supercooled glasses.

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